



Electrochemical and Mechanical Properties of Surface Films and Their Relation To the Stress Corrosion Cracking of Steels

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ABSTRACT

Electrochemical and mechanical techniques were used to grow films and study some of their properties. Polarization curve measurements were performed on Cr-Mo alloy steel specimens in carbonate/bicarbonate solutions at 75 °C. Films were grown at -700, -725, -750, -800 and -850 mV at 75 °C. It was found that stress corrosion cracking (SCC) was most likely to occur between -650 and -750 mV (SCE). AC impedance and nano-hardness of the films were measured. The results showed that the impedance of the films grown within (SCC) range had diffusion control behavior which indicated passivity whereas the impedance of the films grown outside the (SCC) range showed charge transfer behavior which meant that they were not passive. This result implies that the passive films might cause SCC in Steels. The films grown within the (SCC) range had relatively high hardness compared to those grown outside the range which indicated that the films grown within the range were brittle and might induce SCC in steels.

1. INTRODUCTION

Stress corrosion cracking (SSC) is cracking due to a process involving conjoint corrosion and straining of a metal, or alloy, due to residual or applied stresses. SCC is an insidious form of corrosion: it is characterized by a marked loss of mechanical strength with little metal loss. The damage is not obvious to casual inspection and SCC can trigger fast mechanical fracture resulting in catastrophic failure of components and structures. Several major disasters have involved SCC, including the rupture of high-pressure gas transmission pipes and the explosion of boilers in power stations and oil refineries (Congleton & Parkins, 1988; and Schütze 1997).

Cracking is often linked to defects in the alloys and is usually associated with the formation of a surface film often composed of oxides. This film is relatively brittle in nature. The growth rate of the film must complement the rate of crack extension in order for the SCC to be sustained. That is because the crack sides must passivate while the metal continues to dissolve at the crack tip, otherwise general corrosion within the crack enclave would lead to

blunting and crack arrest. If the passivation rate is too fast, dissolution at the crack tip is prevented, and again cracking would stop. The nature of the oxide film and its passivation rate are strongly influenced by the electrode potential (Stahle et al., 1979; Parkins, 1972; and Fontana, 2005).

Previous researches (Congleton & Parkins, 1988; Newman & Procter, 1990; Congleton et al., 1985; Turnbull, 1993; Katada & Nagata, 1985; and Nazarov et al., 2017) showed that the rate of cracking of pure iron is strongly potential dependent and is confined to a narrow potential region at lower temperatures. However, mild steel exhibits a lower degree of potential dependence such that the rate of cracking is decreased under anodic potentials but is not confined to a potential region. The fact that the rate of cracking is to some extent potential dependent indicates that the nature of the oxidized surface of the steel is important in influencing the cracking initiation and propagation. It is shown in the literature that the properties of the passive films may be important in understanding the role of the films in SCC in steels. Thus it would be useful to conduct an electrochemical and mechanistic study of films across a wide temperature range in aqueous environments to elucidate this role.

2. EXPERIMENTAL

2.1 Material and Environment

The specimens used in all experiments were made of Cr-Mo low alloy steel. The specimens were polished to 1200 grit silicon carbide paper and then rinsed with deionized water and methanol just before immersing in the test solution. All experiments were carried out in solutions composed of 1.0 M NaHCO_3 and 0.5 M Na_2CO_3 known to cause SCC in steels. The pH of the solutions was around 9.5. The experiments were carried out at 75 °C.

2.2 Polarization Curve Measurement

Potentiodynamic polarization curves were measured using a (Solatron 1286 Electrochemical Interface Potentiostatic/Potentiodynamic Instrument). The test cell was 1.0 liter flask with a round bottom which could be securely mounted on a heater, if required. The flask had several ports to allow the electrodes and other devices to be immersed in the solution. Sufficient amounts of solutions were used to ensure that all electrodes were immersed and the composition of electrolyte was maintained during testing. A platinum electrode was used as a counter electrode. All potentials were measured against a saturated calomel electrode (SCE)



which was connected to the test cell by means of a salt bridge. All potentials in this work are referenced to saturated calomel electrode (SCE) unless stated otherwise. The specimens (working electrodes) were threaded to a rod which was insulated from the solution and the specimen. When the test cell was set up, the specimens were held at a static potential of -1100 mV for 50 seconds in order to remove any oxides that might have been formed due to contact with air. Then, the potential sweep was started at -1100 mV and swept in the positive direction to 0 mV. Fast and slow sweep rates of 10 mV/sec and 0.1 mV/sec were used.

2.2 Growing of Passive Films on Specimens

Films were grown at -700, -725, -750 and -800 mV. The test cell used was the same one used for polarization curve measurements. The specimens were held at a static potential of -1100 mV for 50 seconds in order to remove any oxides that might have been formed due to contact with air. Then, the specimens were held at static potentials of -700, -725 and -750 mV (SCE) until the current density had dropped to zero (i.e. complete passivation had occurred). The specimens were also held at -800 mV (SCE) for two hours but did not completely passivity. The specimens were then removed from the solution, rinsed with deionized water and methanol, and stored in a desiccator to prevent contact with moisture until they were analyzed later. A separate experiment was conducted at each potential.

2.3 AC Impedance

AC impedance of the films grown different potentials at 75 °C was measured using a (Solatron 1286 Electrochemical interface Potentiostatic/Potentiodynamic Instrument). The AC impedance of the films was measured at open circuit, anodic and cathodic potentials. The measurements were started when the open-circuit potential became constant and at a frequency of 0.1 Hz and swept to 100 kHz. A sinusoidal voltage amplitude of 10 mV was selected for all AC impedance measurements.

2.4 Nano-Hardness

The hardness of the films was determined at different contact depths in order to detect and limit the substrate interaction.

3. RESULTS AND DISCUSSION

3.1 Polarization Curve Measurements

Fast and slow polarization measurements were used to determine the potential region where stress corrosion cracking may occur. The fast and slow sweep polarization curve at 75°C is shown in Figure 1. In the fast sweep, film formation conditions were minimized, but the slow sweep was performed to allow film formation. It can be seen that curves in the both sweeps are similar in the potential region more negative than -760 mV . The drop in current density in the cathodic potential region (more negative than free corrosion potential) was almost the same in both sweep rates. The increase in current densities above the free corrosion potential represented metal dissolution. At about -760 mV , current density started to drop sharply in the case of slow sweep rate indicating film formation. It is clear that the maximum difference in current densities between the two sweeps lies between -650 and -750 mV . This is the region where the metal alloy is most likely to be susceptible to SCC in this environment.

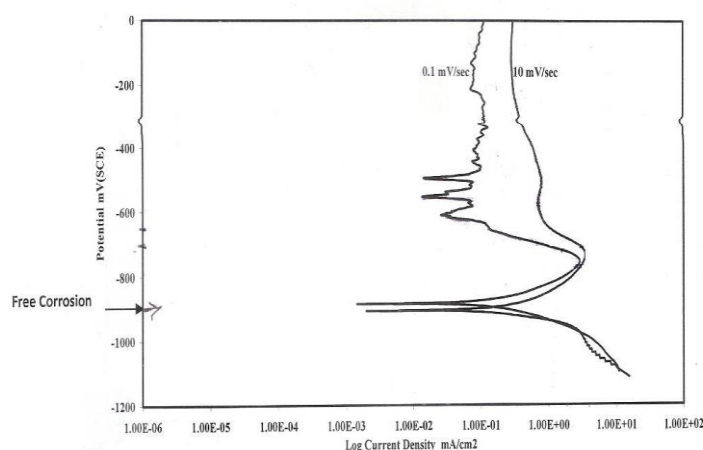


Figure 1: Polarization curve at 75°C

3.2 Growing of Films

The current densities of the films grown at 75°C dropped to zero in less than 2500 seconds at -750 , -725 and -700 mV (SCE) which implied that the films formed at these potentials were completely passive. The films formed at -800 mV was not completely passive. This result was expected because this potential is in the metal dissolution region as shown in Figure 1. At this region, dissolution is too fast and general corrosion rather than SCC occurs. This means that SCC may occur in the potential region at which completely-passive films formed (11, 12) . At 75°C , the findings are in agreement with polarization curves.

3.3 AC Impedance

As shown in Figures (2 and 3), the AC impedance of the films grown within the SCC range had diffusion control behavior which means that they were passive. On the other hand, the AC impedance of the films grown out of the SCC range showed charge transfer semi-circle which indicates that they were not passive. These results agree with the polarization curve measurements which supports the idea that the films must be passive to induce SCC in steels.

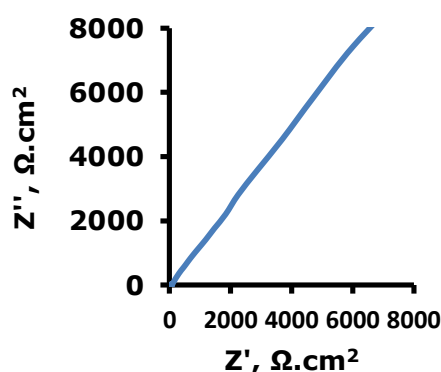


Figure 2: Passive, showing diffusion control

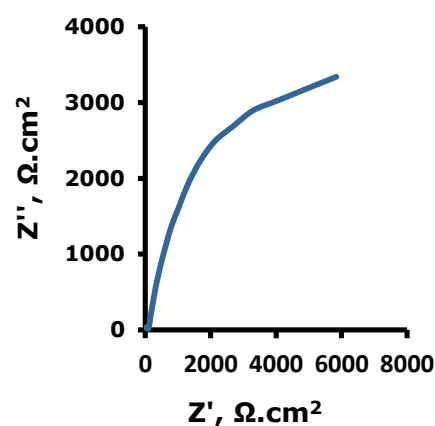


Figure 3: Charge-Transfer semi-circle

3.4 Nano-Hardness

As shown in Figure 4, films grown within the SCC range had relatively high hardness which means that they were brittle. Brittleness is an important property of the films which might trigger SCC in steels. In contrast, the films grown out of the SCC range were not hard enough which indicates that they were not brittle so they might not induce SCC. These results are in an agreement with the polarization curve and AC impedance.

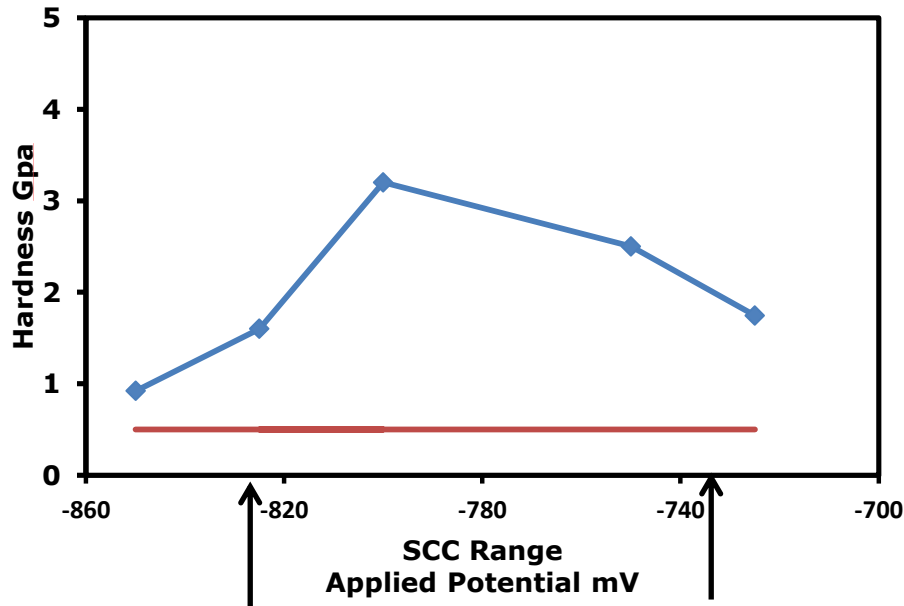


Figure 4: Nano-Hardness of films grown within and outside the SCC potential range in the Carbonate Environment at 75 °C.

4. CONCLUSIONS

The analyses performed in this study lead to the following conclusions:

- The polarization curves indicate that stress corrosion cracking is likely to occur in the potential range -650 to -750 mV .
- Films formed at -700, -725 and -750 mV and 75 °C were completely passive, but the film formed at -800 mV was not.
- The AC impedance of the films formed within the SCC range showed diffusion control which indicates passivity whereas the impedance of the films formed out of the SCC range showed charge-transfer semi-circle which means that they were not passive.
- The films formed within the SCC range had relatively high hardness which meant that they were brittle and might induce SCC in steels.
- The films formed out of the SCC range had relatively low hardness which indicated that they were elastic and might not induce SCC.

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